

(1)

Maxwell's Boltzmann function for distribution of particle : (M-B distribution law):

The fundamental postulate of M-B statistics are:-

(1) The particles of the system are identical but distinguishable.

(2) The system is isolated, so that the total no. of particle is constant.

$$\text{i.e. } \sum n_i = \text{Constant}$$

$$\text{or } \sum dn_i = 0 \rightarrow (1)$$

(3) The particles are non interacting, so that the total energy of the system is constant. i.e

$$\sum E_i n_i = \text{Constant}$$

$$\text{or } \sum E_i dn_i = 0 \rightarrow (2)$$

Consider a system of N identical but distinguishable molecules. Let n_1, n_2, \dots, n_k be the number of molecules having energies E_1, E_2, \dots, E_k respectively.

The total probability of distribution of molecules

$$P = N! \prod_{i=1}^k \frac{g_i^{n_i}}{n_i!} \rightarrow (3)$$

where g_i be the priori probability for molecule of energy E_i .

(2)

Taking logarithm we get

$$\begin{aligned}\log_e P &= \log_e N! + \sum \log_e \frac{g_i}{n_i!} \\ &= \log_e N! + \sum n_i \log_e g_i - \sum \log_e n_i!\end{aligned}$$

from Stirling's formula we get $\rightarrow (4)$

$$\ln n! = n \ln n - n$$

Now applying this formula in equation
(4) we get,

$$\begin{aligned}\ln P &= N \ln N - N + \sum n_i \ln g_i \\ &\quad - \sum n_i \ln n_i + \sum n_i\end{aligned}$$

$$\Rightarrow \ln P = N \ln N + \sum n_i \ln g_i - \sum n_i \ln n_i \rightarrow (5)$$

$$(\because \sum n_i = N)$$

Now differentiating diff. it we get

$$\begin{aligned}d(\ln P) &= - \sum n_i d \ln n_i - \sum d n_i \ln n_i + \\ &\quad \sum d n_i \ln g_i \\ (\text{Here } N \ln N &= \text{constant}) \text{ and } (\ln g_i = \text{constant}) \\ &= - \sum n_i \frac{1}{n_i} d n_i - \sum d m_i \ln n_i \\ &\quad + \sum d n_i \ln g_i\end{aligned}$$

$$= - \sum d n_i - \sum d n_i \ln n_i + \sum d n_i \ln g_i$$

$$= - \sum d n_i \ln n_i + \sum d n_i \ln g_i (\because \sum d n_i = 0) \rightarrow (6)$$

(3)

In equilibrium the probability of distribution of molecules are maximum.

thus $d(\ln P) = 0$.

$$\therefore \textcircled{6} \Rightarrow -\sum d n_i \ln n_i + \sum d n_i \ln g_i = 0$$

$$\Rightarrow -\sum \left(\ln \frac{n_i}{g_i} \right) d n_i = 0 \rightarrow \textcircled{6}$$

$$\Rightarrow \sum \left(\ln \frac{n_i}{g_i} \right) d n_i = 0 \rightarrow \textcircled{7}$$

Consider α and β be the lagrangian undetermined multipliers which are independent of n_i . So multiplying eqn ① by α and eqn ② by β and adding with eqn ⑥ we get

$$\alpha \sum d n_i + \beta \sum E_i d n_i + \sum d n_i \ln \frac{n_i}{g_i} = 0$$

$$\Rightarrow \sum \left(\alpha + \beta E_i + \ln \frac{n_i}{g_i} \right) d n_i = 0$$

$$\therefore \alpha + \beta E_i + \ln \frac{n_i}{g_i} = 0$$

$$\Rightarrow \ln \frac{n_i}{g_i} = -(\alpha + \beta E_i)$$

$$\Rightarrow \frac{n_i}{g_i} = e^{-(\alpha + \beta E_i)}$$

Here $f(E_i) = \frac{n_i}{g_i} = e^{-(\alpha + \beta E_i)}$ is called

M-B distribution function. It gives the no. of particles per state of the system.

(4)

$$n_i = \frac{g_i}{e^{\alpha + \beta E_i}}$$

This is the most probable distribution of molecules among the various individual energy states. This law is known as Maxwell-Boltzmann distribution law.

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